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(54) CELLULOSE ACETATE HOLLOW FIBER SEPARATION MEMBRANE

(57)Abstract:
PURPOSE: To obtain a cellulose acetate hollow fiber separation membrane which maintains high penetration velocity even under low pressure and has high strength by specifying the property of a three-dimentional meshlike porous part and a void part, specifying the ratio of both parts and making a film surface fine and a film thickness within a specific range.
CONSTITUTION: The section of the hollow fiber membrane is composed substantially of the three-dimentional meshlike porous part having 0.05-1μm average pore size and the void part having 10-200 μm size, and the area ratio occupied by the void part to the total section of the membrane is within the range of 5-40%. Moreover, the cellulose acetate hollow fiber separation membrane has the fine film surface having 0. 001-0.05μm surface average pore size at more than one side of the internal and external surface of the hollow fiber, and film thickness is within the range of 50-500μm.

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CLAIMS

[Claim(s)]
[Claim 1] The cross section of a hollow fiber is 0.05-1 micrometer substantially. A three-dimensions mesh-like porosity part, and 10-200 which have an average aperture mum It consists of a void part of magnitude. It is in the range whose area which the void part to the total cross section of this film occupies is 5 - 40%. To and at least one side of a hollow filament inside-and-outside front face 0.001-0.05 micrometers It has a precise film front face with a surface average aperture, and thickness is 50-500. mum Cellulose acetate hollow filament demarcation membrane characterized by being in the range.
[Claim 2] The cellulose acetate hollow filament demarcation membrane according to claim 1 to which the three-dimensions mesh-like porosity part of a membranous cross section is gradually characterized by having the inclination structure which becomes small by the aperture at a target toward one [at least] inside-and-outside front-face side side.
[Claim 3] **** fracture point reinforcement is 30kg/cm2. Cellulose acetate hollow filament demarcation membrane according to claim 1 or 2 to which a **** and **** fracture point ductility are characterized by a certain thing 20% or more above.
[Claim 4] The transmission rate of the pure water in the differential pressure between film of 1kg/cm2 and the temperature of 25 degrees C is 150. Cellulose acetate hollow filament demarcation membrane given in any 1 term of claims 1-3 characterized by a certain thing a liter/(m2, hr) above.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to a cellulose acetate hollow filament demarcation membrane available to water treatment, such as water purification-ized processing and waste water treatment.
[0002]
[Description of the Prior Art] In recent years, in separation actuation, progress of the technique using a demarcation membrane is remarkable, and is put in practical use for various kinds of applications.
[0003] As a material of this demarcation membrane, although a polysulfone system, a polyacrylonitrile system, a polyvinyl alcohol system, polyimide system resin, etc. are used, especially polysulfone system resin is excellent in physical and chemical property, such as thermal resistance, acid resistance, and alkali resistance, and is briskly used from the point also with easy film production, for example.
[0004] However, in order that water permeability may decrease remarkably if the film is once dried when the demarcation membrane which consists of a hydrophobic material like polysulfone system resin is used for a water treatment application, it has the fault that humid-ized processing must be carried out on the occasion of a reuse. Moreover, if it filters using such a hydrophobic demarcation membrane, processed underwater a high polymer, colloid, a particle, etc. start membranous contamination and blinding (film fouling) that it is easy to stick to the interior of a film surface or a pit, there is a problem of filtration velocity falling remarkably with time, and JP,59-196321,A, JP,59-196322,A, JP,57-174104,A, etc. are proposed as an approach of improving a hydrophilic property.
[0005] On the other hand, it has the description that the fall of the filtration velocity in a drainage system with the passage of time of the demarcation membrane using the cellulose system resin which is the hydrophilic macromolecule material known conventionally is small. For example, since the fall of a film transmission rate is small and there is little adsorption of plasma, protein, etc., the regenerated-cellulose film is used as hemodialysis film. Moreover, the unsymmetrical reverse osmotic membrane made from cellulose acetate is similarly used as a seawater desalination application for many years.
[0006] However, in the case of the hemodialysis film which uses such cellulose system resin as film material, in order to raise a plasma separation rate, thickness is made thin, and generally, the bursting pressure has become a small thing. Moreover, the membranous separation barrier layer of the reverse osmotic membrane which can separate comparatively small matter and low molecular weight compound of ion and particle diameter is very precise, since the film aperture is very small, membranous seepage resistance is large [a reverse osmotic membrane], therefore its water penetration rate is small. It is an actuation pressure in order to increase a water penetration rate using the film which has the precise structure which generally starts, although there is a thing of an indication in JP,58-24164,B etc. as a high performance reverse osmotic membrane 10kg/cm2 It must make it the above high pressure, and energy cost not only increases, but the consolidation of the film is carried out during filtration operation, and the problem of bringing about the fall of a water penetration rate or causing mechanical film breakage arises.
[0007]
[Problem(s) to be Solved by the Invention] For this invention, an actuation pressure is 2kg/cm2 in

order to conquer the various faults of the conventional technique mentioned above. It aims at offering the good cellulose acetate hollow filament demarcation membrane of the balance which could maintain the high water penetration rate over the long period of time also under the following low voltage, and was excellent in the mechanical strength.
[0008]
[Means for Solving the Problem] this invention persons reached this invention, as a result of repeating examination wholeheartedly, in order to attain said purpose.
[0009] That is, for this invention, the cross section of a hollow fiber is 0.05-1 micrometer substantially. A three-dimensions mesh-like porosity part, and 10-200 which have an average aperture mum It consists of a void part of magnitude. It is in the range whose area which the void part to the total cross section of this film occupies is 5 - 40%. To and at least one side of a hollow filament inside-and-outside front face 0.001-0.05 micrometers It has a precise film front face with a surface average aperture, and thickness is 50-500. mum It is related with the cellulose acetate hollow filament demarcation membrane characterized by being in the range.
[0010] Moreover, as for the hollow fiber of this invention, the three-dimensions mesh-like porosity part of a membranous cross section may have [the aperture] gradually the inclination structure which becomes small on the target toward one [at least] inside-and-outside front-face side side.
[0011] what is in the range whenever [acetylation / whose] is usually 40 - 62% although there will be no limit in whenever [acetylation] if the cellulose acetate used for this invention is dissolved in the usual organic solvent -- the thing of 55 - 62% of range is preferably suitable. moreover, average degree of polymerization 100-360 -- desirable -- 140-280 A thing is used.
[0012] In this invention, as a film production solution for manufacturing a hollow filament demarcation membrane, it is desirable to dissolve the weight of cellulose acetate in a polar organic solvent so that it may become 10 - 30% of the weight to the AUW of a film production solution in order to obtain the target film. It is 15 - 23 % of the weight more preferably. As a polar organic solvent, they are 1, 4-dioxane, and dimethyl sulfoxide, for example N.N-dimethylformamide Although a N-methyl-2-pyrrolidone, 2-pyrrolidone, etc. can be illustrated, it is not limited to especially these. Moreover, especially, although nonsolvents, such as ethylene glycol and a polyethylene glycol, can be added in addition to the above-mentioned solvent, in order to acquire the target membrane structure, it is desirable to use ethylene glycol as an additive. Since these additives also increase the viscosity of a film production solution with the increment in the addition, a desirable addition is 1 - 30 % of the weight from the point of spinning nature to the AUW of a film production solution. Moreover, addition of plasticizers, such as phosphoric-acid triethyl and diethylene-glycol wood ether, does not obtain and have the desirable water penetration rate which produces and needs fault -- a compact layer becomes thick or generation of a void is barred.
[0013] In manufacturing a hollow filament demarcation membrane from the above-mentioned film production solution, the manufacturing method of the demarcation membrane used from the former is employable. That is, extrude a film production solution from the outer tube of a double pipe mold nozzle, and internal coagulation liquid is made to flow out of an inner tube, by dryness-and-moisture type spinning or wet spinning, it can be made to be able to solidify in a coagulation bath and a hollow fiber can be obtained. Whenever [internal coagulation solution temperature], or coagulation bath temperature has desirable 30-80 degrees C, and at less than 30 degrees C, a compact layer generates thickly on a film front face, the target transmission rate is not obtained, and if it exceeds 80 degrees C, a normal hollow filament will not be obtained. **** distance on the nozzle regurgitation side in the case of dryness-and-moisture type spinning, and the front face of a coagulation bath What is necessary is just to introduce into a coagulation bath, after passing the inside of 0.2-second or more air, that it is good and 0.1-50cm is suitable for 0.5-30cm, and.
[0014] Although these two or more sorts of mixed solutions, such as the water and ethylene glycol which are the nonsolvent of cellulose acetate, and a polyethylene glycol, or the mixed liquor of above-mentioned polar organic solvents and such nonsolvents is used as the internal coagulation liquid used for film production, or a coagulation bath, especially, film production nature is good, it is the point that the average aperture made into the purpose is obtained, and the combination of water or water, and a polyethylene glycol is desirable. If the weight ratios of water/polyethylene glycol are 70 / 30 - 99/1 in the case of the combination of water and a polyethylene glycol, film production nature and

membraneous ability can be balanced and it is desirable. Furthermore, as a polyethylene glycol, it is average molecular weight. About 200 thing is desirable.
[0015] the fine hole of a compact layer with which the three-dimensions mesh-like vesicular structure in this invention is formed in a hollow fiber front face -- an aperture -- large -- substantial -- 0.05-1 micrometer The structure where the opening which has size was formed in the interior of the film as the shape of a three-dimensional mesh can be pointed out, and big physical reinforcement and big ductility can be given to a hollow filament demarcation membrane.
[0016] Moreover, it is still larger than the opening of the shape of an above three-dimensions mesh, and the void in this invention is 10-200 substantially. mum A hole is meant. The area which a void occupies has [that it should just exist in extent which does not lower a membranous mechanical strength although a void can make a water penetration rate increase by existing in the interior of the film moderately] that more desirable whose 5 - 40% is in 15 - 30% of range preferably to the hollow filament cross section from the balance of a water penetration rate and a membranous mechanical strength.
[0017] Moreover, the suspension particle in a processed liquid trespasses upon the interior of the film, and the hollow filament demarcation membrane of this invention is blockaded, in order to prevent bringing about reduction of a water penetration rate, it has a compact layer in either [at least] a membranous internal surface or an outside surface, but when the surface average aperture of this compact layer is small, a practical water penetration rate is not obtained. for this reason, the surface average aperture of a compact layer -- substantial -- 0.001-0.05 micrometers it is -- ****ing -- desirable -- 0.005-0.03 micrometers It is good, and the thing in the range makes it a cut off molecular weight, and is equivalent to 10,000-500,000.
[0018] Moreover, the thickness of the hollow filament demarcation membrane of this invention is 50-500, in order to obtain a bigger water penetration rate than bigger film reinforcement. mum It is adjusted to the range. Thickness is 50 micrometers. In the following, it is inferior to practical strength, and is conversely. 500 micrometers It is from a water penetration rate becoming small and practicality being missing, although film reinforcement increases if it exceeds. 100-400 mum The thing in the range is good.
[0019] In order for the hollow filament demarcation membrane obtained by this invention to maintain endurance over a long period of time **** fracture point reinforcement is 30kg/cm2. It is desirable to be above and for **** fracture point ductility to be 20% or more. Moreover, in order to obtain energy cost comparable as water treatment facilities, such as the conventional water purification-ized processing and waste water treatment, and permeable ability, the transmission rate of the pure water in the differential pressure between film of 1kg/cm2 and the temperature of 25 degrees C It is desirable that they are 150l. / (m2, hr) above.
[0020] In addition, occupancy area % of the magnitude of a three-dimensions mesh-like vesicular structure and the diameter of a hole of a void and the void per film cross-sectional area is evaluated with an electron microscope photograph. Moreover, the surface average aperture of a compact layer is estimated by an electron microscope photograph and the cut off molecular weight.
[0021]
[Example] Below, based on an example, this invention is explained more at a detail.
[0022] In addition, the engine performance of the hollow filament demarcation membrane of this invention measured a water penetration rate, a cut off molecular weight, bursting pressure, and **** fracture point reinforcement and ductility by the following approaches, and evaluated them.
[0023] (1) It is 1kg/cm2 with 25-degree C pure water to the hollow fiber of 50cm of water penetration rate effective length. Water pressure was poured from the inside and the amount of transmitted pure water was measured. (internal-surface product criteria) .
[0024] (2) Various protein with which cut-off-molecular-weight molecular weight differs was made into the standard solute, each rate of exclusion to the film was measured, the relation between molecular weight and the rate of exclusion was plotted in the graph, and it was made into the cut off molecular weight from the obtained rate curve of molecular weight exclusion in quest of the molecular weight equivalent to 95% of rates of exclusion.
[0025] (3) One end of the hollow fiber of 30cm of bursting pressure effective length was closed, and the pressure which flowed and exploded nitrogen gas was measured with the pressure gage with the

highest **** from another side.
[0026] (4) It is the fracture point reinforcement at the time of performing [the hollow fiber test piece of **** fracture point reinforcement and 5cm of ductility effective sample length] a tension test for a crosshead by part for 10mm/the sample cross section of 1cm 2 It converted into the hit and the elongation was measured.
[0027] 20 % of the weight (whenever [acetylation]: 56.1%, average degree of polymerization 180, and Daicel Chemical Industries, Ltd. make) of example 1 cellulose acetate, and 20 % of the weight of ethylene glycol, the film production solution of 60 % of the weight (NMP) of N-methyl-2-pyrrolidones -- a double pipe mold -- while carrying out the regurgitation from the outer tube of a mouthpiece, 90 % of the weight of water and the mixed solution of 10 % of the weight of polyethylene glycols (PEG-200: Sanyo Chemical Industries, Ltd. make) were breathed out as internal coagulation liquid from the inner tube. It is made to solidify from both the front face in a 50-degree C coagulation bath, after passing through the inside of 2-second interspace mind, next, it is immersed and desolventization is carried out underwater, and it is a bore. The hollow filament demarcation membrane whose area which the void part to the total cross section occupies with 0.8mm and the outer diameter of 1.3mm is 20% was obtained. Aging of the water penetration rate of a transparency experiment according the evaluation result of the obtained film to river water is shown in Table 1 and 2 at drawing 1 . This filtration experiment is a cross-flow-filtration system which performs a back wash periodically, and is filtration pressure. 0.5kg/cm2, back-washing pressure force 1.0kg/cm2 and a back wash were performed for 45 seconds by 1 time of frequency in [filtration time amount] 30 minutes. Measurement initiation The water penetration rate held the initial engine performance 70% or more 100 days after. Moreover, scale factor of the obtained film cross section A 200 times as many electron microscope photograph as this is shown in drawing 2 .
[0028] The hollow fiber was manufactured like the example 1 except having made coagulation bath temperature into 70 degrees C using 19 % of the weight of cellulose acetate, 20 % of the weight of ethylene glycol, and the film production solution of 61 % of the weight of NMP(s) in example 2 example 1. The evaluation result of the obtained film is shown in Table 1 and 2.
[0029] It sets in the example 3 example 1, and they are 80 % of the weight of water, and a polyethylene glycol as internal coagulation liquid. (PEG-200) The hollow fiber was manufactured like the example 1 using 20% of the weight of the mixed solution except having made coagulation bath temperature into 70 degrees C. The evaluation result of the obtained film is shown in Table 1 and 2.
[0030] The hollow fiber was manufactured like the example 2 using the film production solution of 18 % of the weight (whenever [acetylation]; 61%, average degree of polymerization 280, and Daicel Chemical Industries, Ltd. make) of example 4 cellulose acetate, and 82 % of the weight of dimethyl sulfoxide except having made the coagulation bath into 40 degrees C. The evaluation result of the obtained film is shown in Table 1 and 2.
[0031] The hollow fiber was manufactured like the example 2 using the film production solution of 20 % of the weight (whenever [acetylation]; 61%, average degree of polymerization 280) of example 5 cellulose acetate, and 80 % of the weight of dimethyl sulfoxide except having used water as internal coagulation liquid. The evaluation result of the obtained film is shown in Table 1 and 2. Moreover, the electron microscope photograph which expanded the internal-surface side in a film cross section to one 10,000 times the scale factor of this is shown in drawing 3 . This photograph shows having the inclination structure where an aperture becomes small on a target gradually as it goes to an internal surface.
[0032] The hollow filament demarcation membrane whose ratio of a void is 44% like an example 1 was manufactured using 18 % of the weight of example of comparison 1 cellulose acetate, 14 % of the weight of cellosolve acetates, 63 % of the weight of NMP(s), and the film production solution of 5 % of the weight of water except having used water as internal coagulation liquid. The evaluation result of the obtained film is shown in Table 1 and 2. When the transparency experiment of the same river water as an example 1 was conducted using the obtained film, leak occurred by mechanical degradation in three weeks.
[0033] The hollow fiber was manufactured like the example 5 using the film production solution of 19 % of the weight (whenever [acetylation]; 56.1%, average degree of polymerization 180) of example of comparison 2 cellulose acetate, 40.5 % of the weight of dimethyl sulfoxide, and 40.5 % of the weight of

phosphoric-acid triethyl except having made coagulation bath temperature into 70 degrees C. The evaluation result of the obtained film is shown in Table 1 and 2. Plasticizer (phosphoric-acid triethyl) By the added system, it turns out that a void does not generate but it becomes the film with a low water penetration rate. An electron microscope photograph 50 times the scale factor of this film cross section of this is shown in drawing 4 .

[0034] Example of comparison 3 polyether-sulphone hollow fiber (Daicel Chemical Industries, Ltd. make; transmission rate 900l./of FUS-0353, a cut off molecular weight 30,000, and pure water (m2, hr)) When the transparency experiment of the used river water was conducted like the example 1, the water penetration rate fell to 10% or less of the initial engine performance in 30 days. Aging of a water penetration rate is shown in drawing 1 . Moreover, a membranous evaluation result is shown in Table 1 and 2.

[0035]

[Table 1]

	ボイド		平均孔径		
	平均長径（μm）	平均短径（μm）	内表面（μm）	外表面（μm）	三次元網目状構造（μm）
実施例1	100	80	0.02	0.03	0.3
実施例2	130	120	0.02	0.03	0.3
実施例3	80	20	0.02	——	0.3
実施例4	110	30	0.02	——	0.2
実施例5	120	30	0.03	0.02	0.6
比較例1	90	30	0.02	0.02	——
比較例2	——	——	0.02	——	0.3
比較例3	45	7.5	0.01	0.3	0.5

[0036]
[Table 2]

	破断点強度（kg／cm²）	破断点伸度（%）	破裂圧力（kg／cm²）	純水透過速度（リットル／（m²・hr））	分画分子量	ボイドの比率（%）	膜厚（μm）
実施例1	35	33	13	600	30万	20	250
実施例2	53	40	21	310	30万	18	270
実施例3	51	37	15	450	20万	18	260
実施例4	54	34	15	350	20万	37	250
実施例5	49	35	15	320	20万	18	250
比較例1	25	16	13	210	30万	44	280
比較例2	51	33	—	20	30万	0	250
比較例3	49	40	—	900	3万	44	150

[0037]
[Effect of the Invention] This invention can maintain a high water penetration rate over a long period of time compared with a hydrophobic hollow filament demarcation membrane. Moreover, it excels in the mechanical strength, and it is stabilized, and water treatment actuation can be performed, and it excels also in endurance.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Aging of the water penetration rate by transparency experiment of the river water using the cellulose acetate film of an example 1 and the polyether sulphone film of the example 3 of a comparison is shown.
[Drawing 2] It is the electron microscope photograph (200 times) in which the configuration of the fiber of the cross section of the cellulose acetate hollow fiber of this invention obtained in the example 1 is shown.
[Drawing 3] electron microscope photograph in which the configuration of the fiber of the cross section of the cellulose acetate hollow fiber of this invention obtained in the example 5 is shown (10,000 times) it is .
[Drawing 4] electron microscope photograph in which the configuration of the fiber of the cross section of the cellulose acetate hollow fiber obtained in the example 2 of a comparison is shown (50 times) it is .

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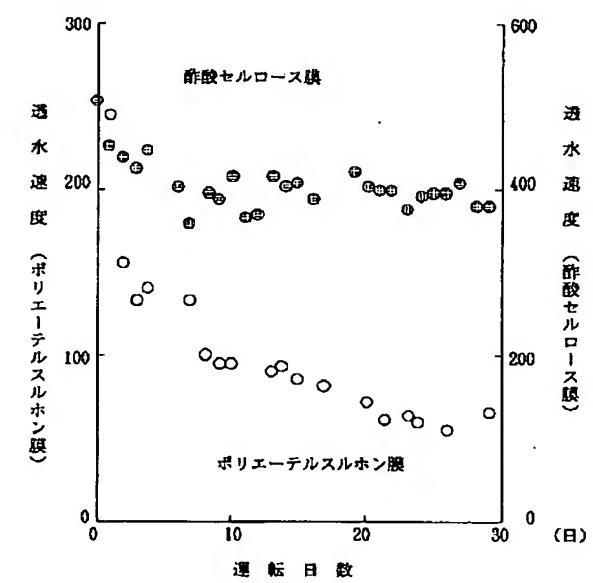
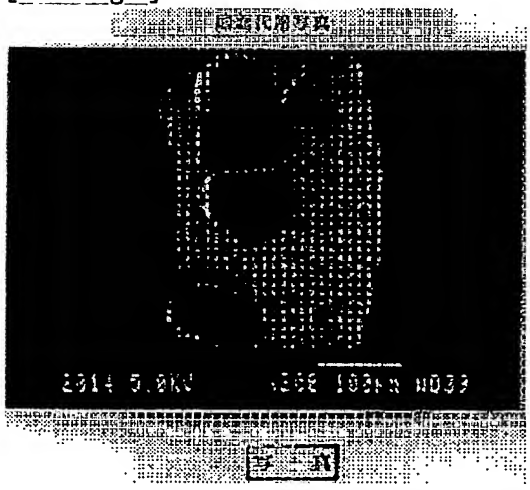
DRAWINGS

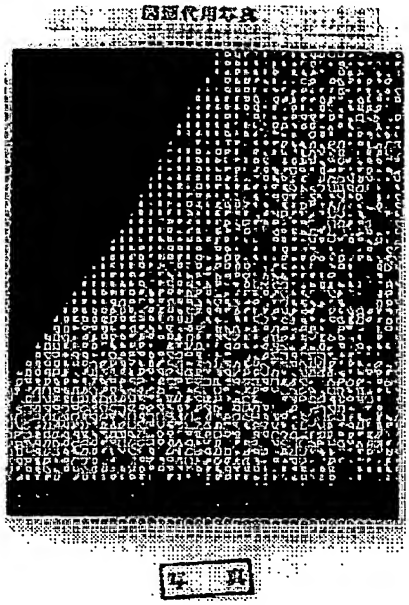
[Drawing 1]



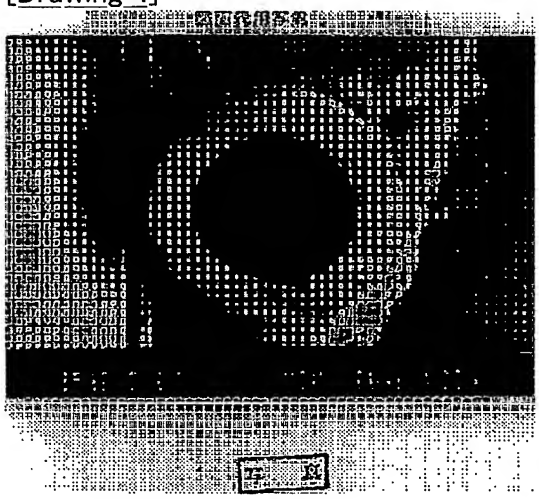
[Drawing 2]



[Drawing 3]



[Drawing 4]



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